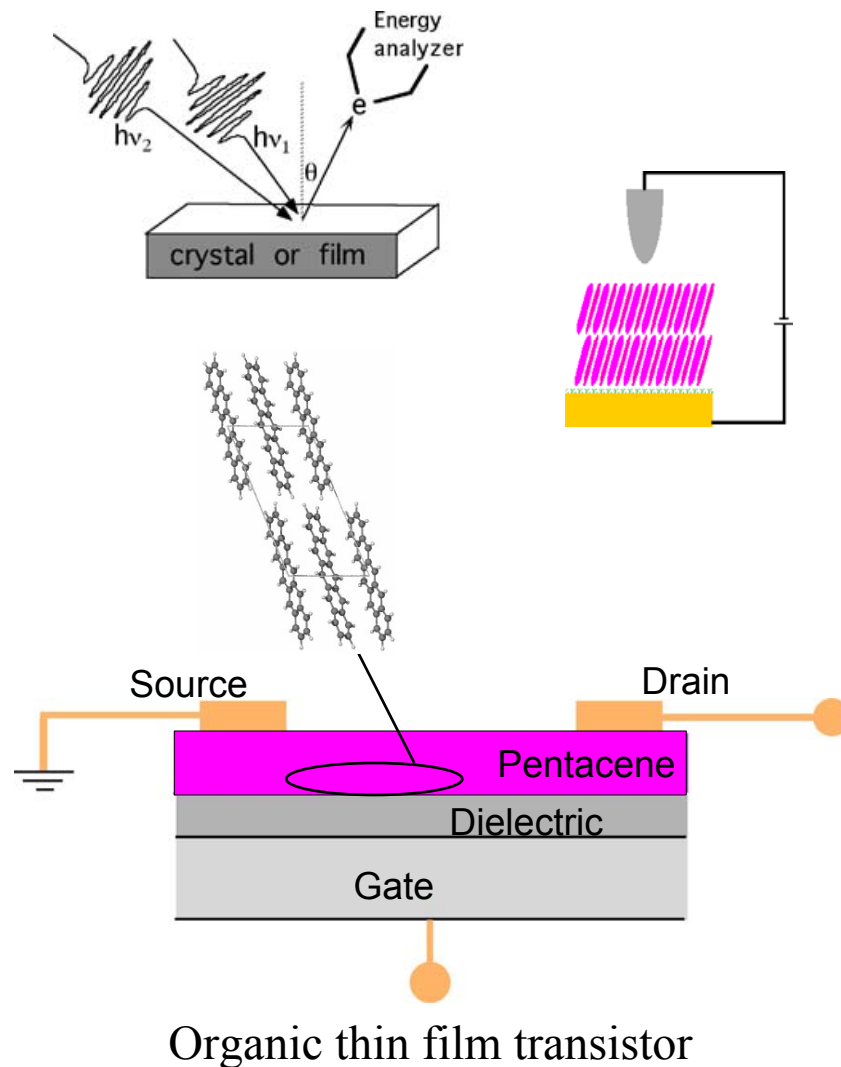


“Electron dynamics in organic semiconductors and at organic metal interfaces”

Xiaoyang Zhu, University of Minnesota, NSF DMR-0238307

Considerable efforts are underway to develop organic semiconductors as viable alternatives to amorphous silicon for thin film electronics. The figure of merit in these materials is the charge carrier mobility. Besides structural factors, such as defect density and domain boundaries, carrier mobility is ultimately determined by the electronic band structure and the strength of electron-nuclear coupling responsible for carrier localization. The central scheme of this proposal is to use femtosecond two-photon photoemission spectroscopy (2PPE), in conjunction with scanning tunneling microscopy (STM) to establish electron dynamics in organic semiconductor crystals, thin films, and at their interfaces with metals, and to probe structure-property relationship in these systems.



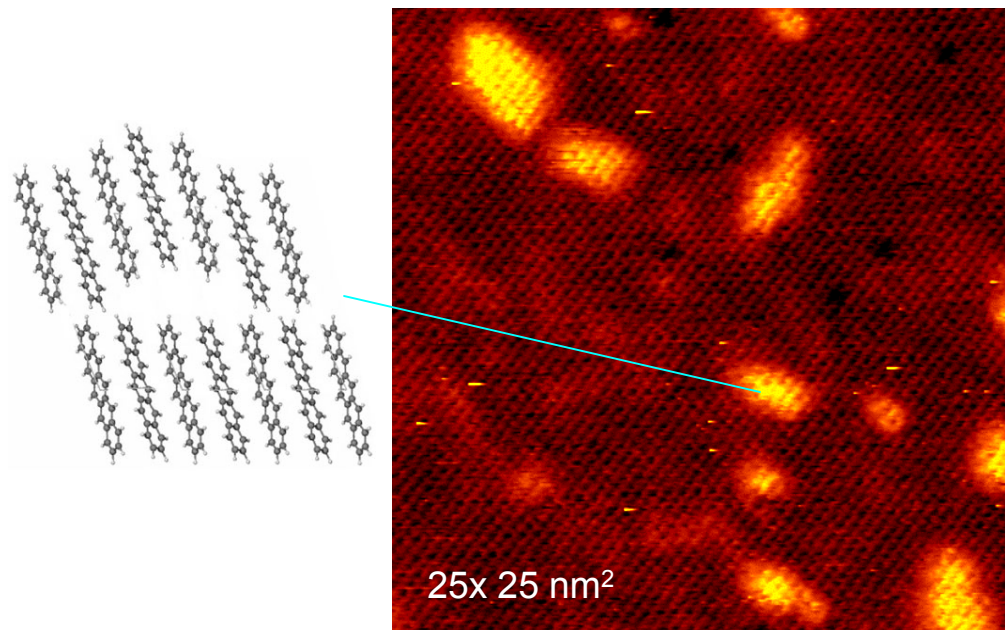
We are addressing two important issues on charge carrier transport in organic semiconductors and at organic-metal interfaces: *structure* and *dynamics*.

On the structure issue, we use STM to directly image defects in crystalline pentacene thin films. We discovered a dominant type of local defect in vapor deposited pentacene thin films resulting from the sliding of pentacene molecules along their long molecular axis while two-dimensional crystallinity in the molecular layer is maintained. These sliding defects are charge carrier traps within each crystalline domain.

On the dynamics issue, we use femtosecond two-photon photoemission spectroscopy (2PPE) to probe a model system: epitaxial thin film of C₆₀ on Cu(111) or Au(111). We demonstrate that 2PPE is capable of probing both excitons and charge-transfer (CT) states at the molecule-metal interface. In particular, we discovered a long-distance electronic coupling between electronic exciton bands in solid C₆₀ and substrate metal bands.

Seeing defects in organic semiconductors

Organic thin film transistors (OTFT) are key components in all molecule-based electronics & optoelectronics. Among the most promising organic semiconductors is pentacene, which has shown the highest charge carrier mobility in OTFTs. The successful development of pentacene based OTFT technology requires a fundamental understanding of structure-property relationship, particularly the relationship of carrier mobility to the nature of defects in pentacene thin films. We have discovered for the first time a predominant type of defects intrinsic to pentacene thin films. These defects result from the sliding of pentacene molecules along their long molecular axis while 2D crystallinity is maintained.

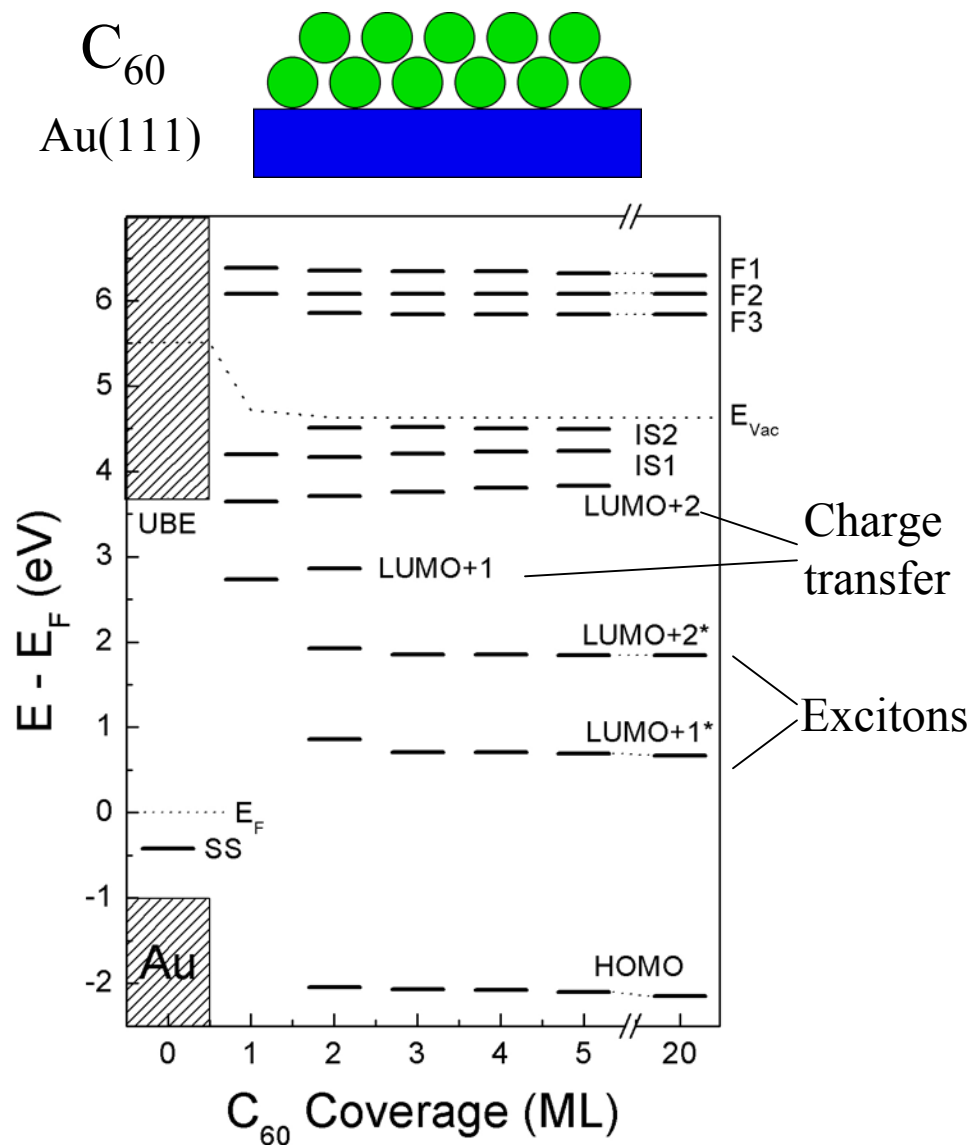


STM image of local defects in a crystalline domain of pentacene. These molecules are arranged with their long molecular axis nearly perpendicular to the surface. The sliding of pentacene molecules along their long molecular axis gives rise to these defects.

OTFTs may serve as driving circuits in active matrix displays, such as organic light emitting diodes (OLEDs) or storage devices in smart cards and RF tags. The advantages of OTFTs include large-area and low-temperature processability, structural flexibility, and low cost. Among the most promising organic semiconductors for OTFTs are polyacenes, particularly pentacene. Pentacene based OTFT has shown the highest charge carrier mobility (μ_{eff}) which rivals that in amorphous silicon devices. In fact, measured μ_{eff} in pentacene thin films has increased over recent years by several orders of magnitude to reach a current value as high as 2 cm²/Vs. Further improvement in μ_{eff} and the successful development of pentacene based OTFT technology requires a fundamental understanding of structure-property relationship, particularly the relationship of carrier mobility to the nature of defects in pentacene thin films. While substantial efforts have been made in reducing charge traps due to impurities and domain boundaries, the nature of local defects within each crystalline domain remained unknown. These local defects may ultimately limit mobility of pentacene OTFTs. We have discovered for the first time a predominant type of local defects intrinsic to pentacene thin films. On a low surface energy substrate, crystalline pentacene thin films grow with the well-known herringbone packing motif and with the ab plane parallel to the surface (step height = 15 Å). Within each crystalline domain, the sliding of pentacene molecules along their long molecular axis gives rise to a high density of defect, while two-dimensional crystallinity is maintained. These local defects are likely intrinsic to thin films of layered organic solids from van der Waals (VDW) epitaxy.

Electronic energy levels and interfacial coupling at molecule-metal interfaces

How electronic energy levels in an organic semiconductor couple to a metal electrode is of critical importance to electronic devices. Two-photon photoemission spectroscopy allows us to map out unoccupied states (excitons and metal-to-molecule charge transfer states), as illustrated by results for a model system: epitaxial C_{60} thin films on Au(111). More importantly, the technique also allows us to *quantify* the strength of electronic coupling between the molecules and the metal electrode.



We have used two-photon photoemission spectroscopy (2PPE) to study the structure and dynamics in model systems: epitaxial films of C_{60} on Cu and Au(111) surfaces. This approach allowed us to map out two type of excited states: excitons and charge-transfer states, as illustrated for C_{60}/Au as a function of film thickness. Lifetime measurements revealed that the excitons in C_{60} are strongly coupled to the metal substrate over long distance. This finding can be described by a direct coupling of the C_{60} electronic exciton band with the substrate metal band.